VISIT…

3
Esters

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I. HISTORY

Prior to the early nineteenth century, the main lubricants were natural esters contained in animal fats such as sperm oil and lard oil, or in vegetable oils such as rapeseed or castor oil. The earliest recorded use of animal fats, to lubricate chariot axles, occurred in 1400 BC. During World War II a range of synthetic oils was developed. Among these, esters of long chain alcohols and acids proved to be excellent for low temperature lubricants. Following World War II, the further development of esters was closely linked to that of the aviation gas turbine. In the early 1960s, neopentyl polyol esters were used in this application because of their low volatilities, high flash points, and good thermal stabilities. Esters are now used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils, and grease formulations. The low toxicity and excellent biodegradability of ester molecules now afford added benefits to those of performance.

II. CHEMISTRY

A. Product Structure

The ester group directly affects the physical properties of a lubricant by lowering the lubricant's volatility and raising the flash point. Strong dipole moments that bind the lubricant together are responsible for these effects. The presence of the ester group also affects other properties, such as:

thermal stability
hydrolytic stability
solvency
lubricity
biodegradability

These properties are discussed at length later in the chapter.

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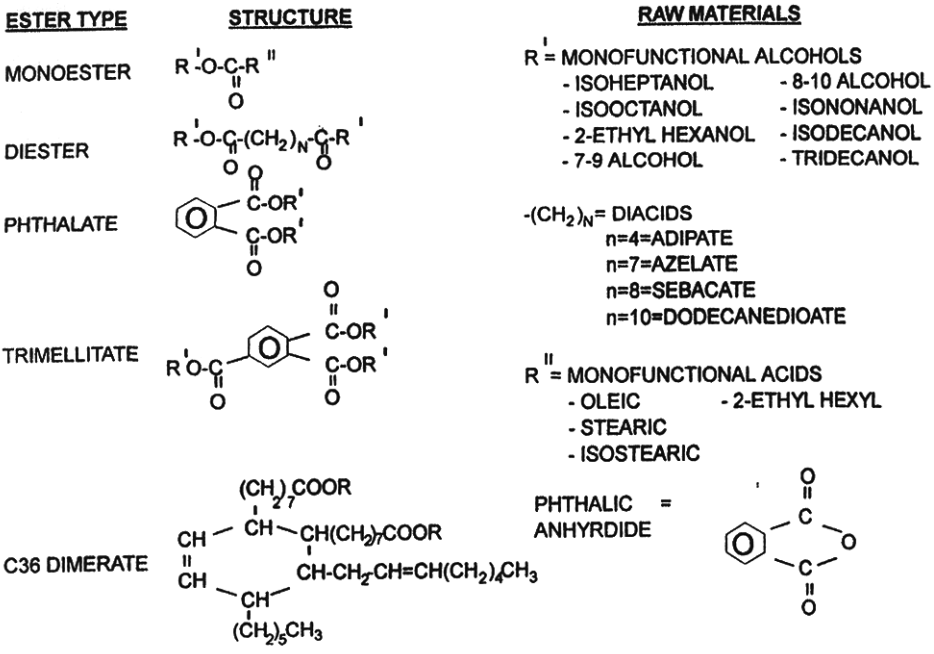

Figure 1 Acid/anhydride-centered ester structures.

There are three main types of ester:

acid/anhydride centered (e.g., monoesters, diesters, phthalates, and trimellitates: Fig. 1)
alcohol centered (e.g., polyols: Fig. 2)
polymeric esters [e.g., polyalkylene glycol (PAG) esters: Fig. 3]

Their physical properties are compared in Table 1.

1. Monoesters

Monoesters are made by reacting a monofunctional acid (e.g., oleic, steric) with a monofunc-tional alcohol (usually between 8 and 13 carbon atoms in length). Monoesters are characterized by their relatively low viscosity. Examples of commercially available monooleate esters with their physical properties are given in Table 2.

2. Diesters

Diesters are made by reacting a linear diacid with a branched monofunctional alcohol. Diesters have very good viscosity indices (VI) and pour points. The reason for this is their "dumbbell" configuration. The linear diacid portion of the diester contributes to the good VI, while the branched ends give the lubricant a good pour point. Since the branched portion of the diester is at the end of a linear portion, the free rotation around the ester linkage is still good. This gives an excellent trade-off between VI and pour point. One disadvantage of diesters is their low molecular weight. This results in a limited ISO range (7–46) coverage. Examples of commercially available diesters are given in Table 3. Their small size combined with their high polarities make them effective solvents. Diesters are often blended with poly(α-olefins) (PAOs) to help additive solubility and to act as seal-swelling agents.

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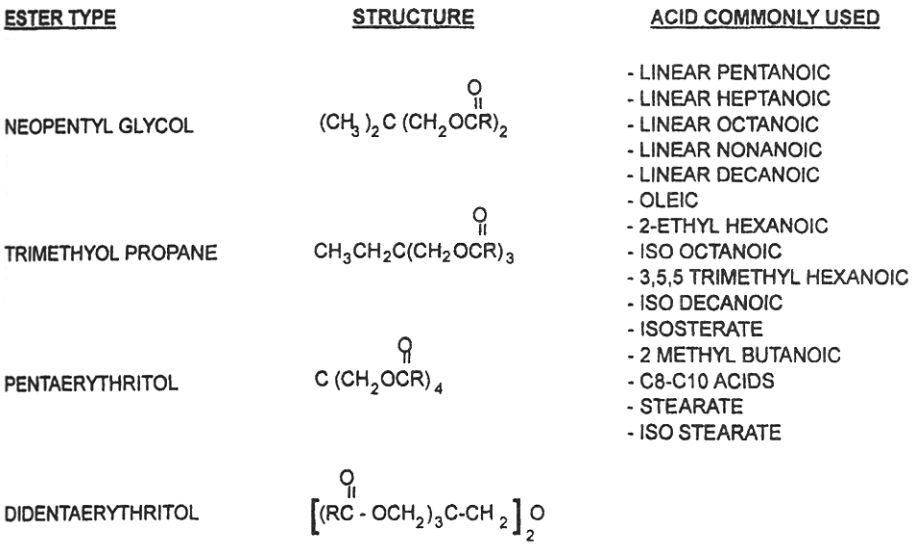

Figure 2 Alcohol-centered ester structures.

3. Phthalates

Phthalate esters are made by reacting phthalic anhydride with a monofunctional alcohol (C_8 to C_{13} in length). Examples of commercially available phthalates and their physical properties are given in Table 4. Phthalic anhydride is used instead of phthalic acid for reasons of cost and/or availability. Phthalate esters are among the most cost-effective of esters, and as such they often replace mineral oil in industrial applications, such as air compressors. Owing to the bulky "basketball-like" shape to the molecule, they can have low pour points or good VIs, but not both. In terms of viscosities they are available in viscosity range ISO 22 to ISO 80. ISO 100 oils are made by blending the ISO 80 oil with a trimellitate.

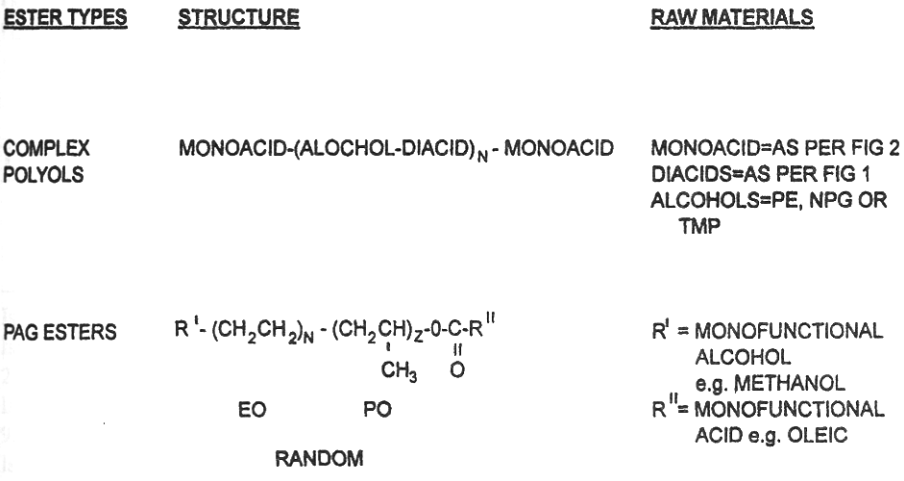

Figure 3 Polymeric esters.

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Table 1 Overview of Ester Physical Properties

	Diesters	Phthalates	Trimellitate	C_{36} Dimerates	Polyols	Polyoleates	Complex polyols
Viscosity at 40°C, cSt	6–46	19–80	46–320	90–184	7–220	46–100	46–460
Viscosity at 100°C, cSt	2–8	3–8	7–20	12–20	2–20	10–15	7–45
Viscosity index	120–160	−ve–90	75–130	120–150	50–140	130–180	130–200
Pour point, °C	−70 to −40	−50 to −30	−55 to −25	−50 to −5	−60 to −9	−40 to +8	−60 to −20
Flashpoint, °C	200–260	200–270	270–300	240–310	250–310	220–280	240–280
Thermal stability	Good	Very good	Very good	Good	Excellent	Fair	Fair
Blodegradability	Good	Fair	Poor	Fair	Excellent	Excellent	Excellent

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Table 2 Summary of Monooleate Physical Properties

	Viscosity (cSt)		Viscosity index	Pour point (°C)
	At 40°C	At 100°C		
Methyl	4.4	1.7	—	−12
Iso butyl	6.0	2.2	219	−50
2-Ethylhexyl	8.0	2.8	238	−35
Isooctyl	9.1	2.9	192	—
Decyl	10.2	3.4	246	−3

Table 3 Summary of Diester Physical Properties

	Viscosity (cSt)		Viscosity index	Pour point (°C)	NOACK at 250°C/h (% loss)[a]	Biodegradability CEC-L-33-A-96 (% in 21 Days)[b]
	At 40°C	At 100°C				
2-Ethylhexyl						
adipate	8.0	2.4	124	−68	44.3	97
azelate	10.7	3.0	137	−64	29.0	99
sebacate	11.8	3.1	126	−60	18.3	96
dodecanedioate	14.3	3.8	168	−57	—	—
Isodecyl						
adipate	15.2	3.6	121	−62	15.5	84
azelate	18.1	4.3	151	−65	9.8	86
sebacate	20.2	4.8	169	−60	6.2	100
dodecanedioate	23.4	5.2	162	−41	4.3	93
Isotridecyl						
adipate	27.0	5.4	139	−51	4.8	92
sebacate	36.7	6.7	141	−52	3.7	80
dodecandiote	40.7	7.6	156	−50	2.9	76

[a] NOACK,
[b] CEC,

Table 4 Summary of Phthalate Physical Properties

	Viscosity (cSt)		Viscosity index	Pour point (°C)	NOACK at 250°C/h (% loss)	Biodegradability CEC-L-33-A-96 (% in 21 days)
	At 40°C	At 100°C				
Isoheptyl	19.0	2.8	−177	−51	21.1	92
Isooctyl	28.8	4.5	39	−42	17.5	69
2 Ethylhexyl	26.4	4.2	21	−43	19.0	64
Isononyl	38.5	5.3	50	−44	11.7	53
9/11 Alcohol	30.0	5.0	87	−52	4.3	88
Isodecyl	45.5	5.8	49	−47	9.2	69
Isotridecyl	80.5	8.2	56	−43	2.6	46

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4. Trimellitates/Pyromellitates

Trimellitates are made by reacting trimellitic anhydride with a monofunctional alcohol (C_8 to C_{13} in length). Examples of commercially available trimellitates and their physical properties are given in Table 5. Trimellitates are often used instead of phthalates if enhanced performance (thermal, elastomeric, lubricity) or higher viscosity is required. They are available in a wide range of viscosities (ISO 46–320). In terms of structure they are quite bulky and, like the phthalates, have poor VI/pour point trade-offs. Trimellitates are very good lubricants, and their high molecular weights make for high flash points and low volatilities.

Pyromellitates are made by reacting either pyromelletic anhydride or pyromellitic acid with a monofunctional alcohol. One commercially available pyromellitate is based on 2-ethyl hexanol (see Table 5). Pyromellitates have very good thermal and elastomeric compatibility properties. Unfortunately, the high cost and poor availability of the raw materials tend to make them very expensive. They are generally used in applications such as high temperature chain oils and greases.

5. C_{36} Dimerates

Dimerates are made by reacting a C_{36} dimer acid (derived from tallow oil) and a monofunctional alcohol. The alcohol most widely used is 2-ethyl hexanol, making an ester that is usually referred to as 3608. This ester is often used in two-stroke oils and has found some use in four-stroke oils. It has the advantage of being an excellent lubricant and has good thermal and oxidative stability. In addition, its stability can be further improved by hydrogenation of the double bonds. Because of the poor biodegradability of dimerates, they are increasingly being replaced by polyols in marine two-stroke engines. Examples of commercially available dimerates and their physical properties are given in Table 6.

6. Polyol Esters

Polyols are made by reacting a multifunctional alcohol with a monofunctional acid (usually C_7 –C_{18}). Examples of commercially available polyols and their physical properties are given in Table 7. They are available in a large range of viscosities (ISO 5–220). Polyols tend to have the same advantages and disadvantages as diesters. They are, however, more hydrolytically and thermally stable than diesters. A rule of thumb is that a polyol is 30–508C more thermally stable than a diester of equivalent viscosity. Because of these performance advantages, sales of polyol esters are expected to grow at a faster rate than diesters. Polyols, however, tend to be more expensive than diesters.

Table 5 Summary of Trimellitate and Pyromellitate Physical Properties

	Viscosity (cSt)		Viscosity index	Pour point (°C)	NOACK at 250°C/h (% loss)	Biodegradability CEC-L-33-A-93 (% in 21 days)
	At 40°C	At 100°C				
Trimellitates						
7/9 Alcohol	48.8	7.3	108	−45	0.9	69
8/10 Alcohol	51.9	8.1	126	−45	0.4	61
9/11 Alcohol	72.5	9.8	116	−45	1.7	3
2-Ethylhexyl	90.2	9.7	82	−36	1.6	14
Isodecyl	144.2	13.0	79	−30	1.0	0
Isotridecyl	305.2	20.4	76	−9	1.6	9
Pyromellitate						
2-Ethylhexyl	172.0	16.3	98	−27	0.4	3

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Table 6 Summary of Dimerate Physical Properties

	Viscosity (cSt)		Viscosity index	Pour point (°C)	NOACK at 250°C/h (% loss)	Biodegradability CEC-L-33-A-96 (% in 21 days)
	At 40°C	At 100°C				
C_{36} dimerate						
2 Ethylhexyl	91.1	12.7	136	−50	0.8	49
9/11 Alcohol	94.9	14.0	151	−15	1.1	78
Isotridecyl	140.0	17.0	132	−27	0.6	30
Hydrogenated C_{36} Dimerate						
2 Ethylhexyl	92.0	12.7	135	−41	0.2	24

7. Other Esters

There are numerous other types of ester, namely:

complex polyols: low molecular weight polymers made from a polyol (neopentylglycol, NPG, trimethyolpropane, TMP, pentaerythritol, PE) and a diacid, and end-capped with either an acid or an alcohol (Table 8)

PAG esters made from a reaction of a polyalkylene glycol (PAG) hydroxyl group with an acid

other polymeric esters (see Chapter 5)

carbonate esters

phosphate esters (see Chapter 4)

citrate esters

Table 7 Summary of Polyol Physical Properties

Polyol type	Viscosity (cSt)		Viscosity index	Pour point (°C)	NOACK at 250°C/h (% loss)	Biodegradability CEC-L-33-A-96 (% in 21 days)
	At 40°C	At 100°C				
NPG						
n-C_7	5.6	1.9	—	−64	—	100
n-C_9	8.6	2.6	145	−55	31.2	97
c-C_8/C_{10}	8.1	2.4	119	−53	32.4	100
TMP						
n-C_7	13.9	3.4	120	−60	11.8	100
n-C_9	21.0	4.6	139	−51	2.3	100
n-C_8/C_{10}	20.4	4.5	137	−43	2.9	96
Oleate	46.8	9.4	191	−39		100
iso-C_9	51.7	7.2	98	−32	6.7	7
PE						
n-C_9	32.2	6.1	140	−7	0.9	100
n-C_8/C_{10}	30.0	5.9	145	−4	0.9	100
iso-C_9	129.2	11.6	70	−22	—	8
n-C_5/*n*-C_7/iso-C_9	33.7	5.9	110	−46	2.2	69
DiPE						
n-C_5/*n*-C_7/iso-C_9	230.0	19.5	120	−15	1.2	—

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Table 8 Summary of Complex Polyol Physical Properties

Complex	Viscosity (cSt) At 40°C	Viscosity (cSt) At 100°C	Viscosity index	Pour point (°C)	NOACK at 250°C/h (% loss)	Biodegradability CEC-L-33-A-96 (% in 21 days)
NPG	40.9	7.7	160	−42	—	98
TMP	115.9	16.5	154	−54	—	94
NPG	132.0	17.1	141	−38	—	92
TMP	274.0	34.7	174	−27	3.7	89
TMP	306.1	35.2	161	−30	2.9	79

Complex polyols have great flexibility. Viscosity can be controlled by the degree of polymerization. Complex esters have the advantages of high biodegradabilities even at high viscosities. This makes them ideal brightstocks for two-stroke applications. Unfortunately, the high number of ester linkages gives these esters a high polarity. This can cause problems with antiwear additives (see Section III, B.3).

PAG esters have the advantage of high VIs and tend to be good lubricants. As with the complex polyols, however, their high polarity may result in compatibility problems with anti-wear additives. Highly ethoxylated PAG esters can be made to be water soluble and as such find application in metalworking fluids and fire-resistant hydraulic fluids. PAG esters tend to be very hygroscopic and can suffer from poor hydrolytic stability.

Citrate esters are used as functional fluids for indirect/direct food use applications.

B. Manufacture of Ester Lubricants

The manufacturing process of esters consists of three distinct stages, namely:

esterification
neutralization
filtration

A schematic of the manufacturing process is given in Figure 4. The production of esters is based on the following reaction: acid 1 alcohol 5 ester 1 water.

For diesters, the reaction can be driven to a high level of completion by using excess alcohol to remove the water of reaction. This usually takes several hours, during which the reaction is monitored by taking samples periodically for acid number determination. The use of an azeotroping agent such as xylene or toluene (to aid water removal) is optional. The acid and alcohol can be reacted directly or in the presence of a catalyst. Possible catalysts include:

sulfuric acid
paratoluenesulfonic acid
tetraalkyl titanate
anhydrous sodium sulfate
phosphorous oxides
stannous octanoate

After the ester has been formed, unreacted acid is neutralized by means of sodium carbonate or calcium hydroxide and is removed by filtration. Typical reaction conditions for titanium catalysts are 2308C in vacuum; acid catalysts require milder conditions, since side reactions

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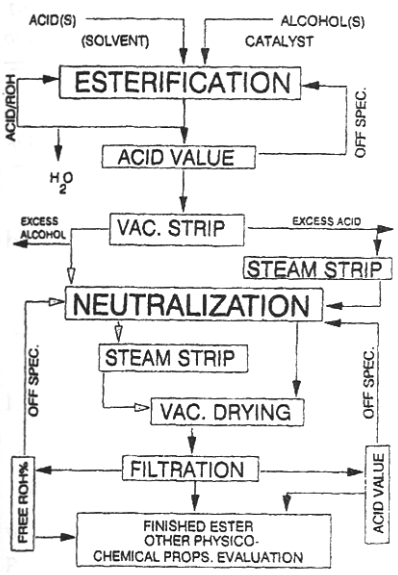

Figure 4 Synthesis of ester lubricants.

(e.g., color formation) become prominent at higher temperatures. A significant amount of alcohol vaporizes along with the water and must be recovered. This is accomplished by condensing the reactor vapors and decanting the resulting two-phase liquid mixture. The alcohol is then refluxed and returned to the reactor.

Polyol esters are made by reacting a polyhydric alcohol, such as neopentyl glycol (NPG), trimethyol propane (TMP), pentaerythritol (PE), or dipentaerythritol (diPE) with a monobasic acid to give a desired ester.

Polyol esters can also be made via a transesterification (alcoholysis) route. Here, monoesters (usually methyl) are transesterified with a neopentyl alcohol in the presence of a catalyst. Catalysts specifically designed to help the transesterification process are now available.

Variations in raw materials can have a major influence on the final physical properties of the ester. For example, the monofunctional alcohols used to make monoesters, diesters, phthalates, trimellitates, and pyromellitates are often mixtures of varying chain lengths, degrees of branching of isomers. Examples of this are:

isotridecanol, which is a mixture of branched carbon chain lengths in the range C_{11} to C_{14} rich in C_{13} alkyl chains

isodecanol, which is a mixture of branched carbon chain lengths C_9 to C_{11}, rich in C_{10} alkyl chains

The degree of branching, the chain length, and the ratio of isomers are highly dependent on the feedstock and catalyst used to make the alcohol. Batches of the same alcohol purchased from different companies or from different plants of same company can vary significantly. Therefore, the typical properties of a given ester may differ from supplier to supplier. This can be seen in Table 9, which compares nominally the same trimellitate made from tridecanol from five different suppliers. A trimellitate was chosen because it would differentiate the most between the different tridecanol sources. Variations also occur with naturally derived acids (e.g., C_8/C_{10} acid is in fact a mixture of C_6, C_8, C_{10}, and C_{12}). The degree of unsaturation (iodine number) should also be checked.

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Table 9 The Effect on the Physical Properties of a Trimellitate of Tridecanol from Several Different Sources

Alcohol source	Viscosity (cSt) At 40°C	Viscosity (cSt) At 100°C	Viscosity index	Flash point (°C)	Pour point (°C)
1	315	19.9	67	298	−7
2	189	16.7	93	268	−17
3	179	16.3	94	—	—
4	366	21.6	65	296	−23
5	320	20.8	73	234	−7

Even if exactly the same raw materials are used, the processing specification can have a major impact on the physical properties, hence on the performance of the ester. The following properties of the ester should be tightly controlled:

residual unreacted acid
hydroxyl number (degree of estrification)
residual unreacted alcohol
cross-contamination of other esters made on plant
residual catalyst
residual neutralizing agents

Guidelines for the recommended levels of these ester properties are listed in Table 10. Note that these are only guidelines and may need to be adjusted depending on the application of use. Several of these factors are discussed in more detail later in the chapter.

III. PROPERTIES AND PERFORMANCE CHARACTERISTICS

Mineral oil base stocks are derived from crude oil and consist of complex mixtures of naturally occurring hydrocarbons. Synthetic ester lubricants, on the other hand, are prepared from raw materials having uniform molecular structures. This uniformity yields well-defined properties that can be tailored for specific applications.

A. Chemical Properties

1. Thermal and Oxidative Stability

The ester linkage is an exceptionally stable one. Bond energy determinations predict that the ester linkage is more thermally stable than the C—C bond.

Oxidation tests show that esters have an oxidative stability similar to or slightly worse than that of mineral oil. The reason for this is that mineral oil contains impurities, which can act as antioxidants. Esters display their superior performance formulated with antioxidants.

Primarily, the oxidative and thermal stability of ester lubricants depend on the following factors:

The presence of hydrogen atoms on β carbons (avoided by use of polyol esters).
The number and type of hydrogens present. In decreasing order of stability, we have—CH_3 . —CH_2— . —CH—. Generally, therefore, (a) linear acid esters are more stable than branched and (b) short chain acids are more stable than long.

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Table 10 The Effect of Specification on the Performance of an Ester Lubricant

Property	Effects	Typical value
Total acid number	Hydrolytic stability Thermal stability Wear	<0.1 mg KOH/g
Hydroxyl number	Hydrolytic stability Deposit formation Foaming Volatility Flash point	<4 mg KOH/g
Iodine number	Thermal stability Color stability Deposit Formation Low temperature flow	As low as possible
Water content	Hydrolytic stability	< 0.1% w/w
Process residuals (e.g. catalyst, neutralizing agents, azeotrope, etc.)	Thermal stability Deposit formation Hydrolytic stability Foaming	<5 ppm metals
Purity	All of the above	

The stability of the alcohol used. In decreasing order of stability the trend is: PE . diPE . TMP . NPG.
Steric effects.
Aromaticity.
(Un)saturation.
Type and dose rate of additives.

The advantages in thermal stability of polyol esters over diesters is well documented and has been investigated on a number of occasions [1–3]. It has been found that the absence of hydrogen atoms on the β-carbon atom of the alcohol portion of the ester leads to superior thermal stabilities. The presence of such hydrogen atoms enables a lower decomposition mechanism to operate via a six-membered cyclic intermediate that produces acids and 1-alkenes (see Fig. 5A). When β-hydrogen atoms are replaced by alkyl groups, this mechanism cannot operate and decomposition occurs via a free radical pathway. This type of decomposition requires more energy and can occur only at higher temperatures (see Fig. 5B). Pentaerythritol-based polyols tend to be more thermally stable than polyols based on TMP, which in turn are more stable than those based on NPG. Generally, short linear chains give better thermal stability than long branched chains. Esters derived from geminal dimethyl acids are the most robust of the branched species, since they are incapable of supporting the β-hydrogen elimination degradation pathway.

The number and type of hydrogen bonds have a major effect on the oxidative stability of esters [4]. The general rule is that the ease of oxidation of carbon–hydrogen bonds follows the order; primary (—CH_3) . secondary (—CH_2—) . tertiary (—CH—), where primary bonds are the most stable. Studies have shown that normal secondary hydrogens can be 15 times less stable than primary hydrogens. Tertiary hydrogens occur at branched positions on the alkyl

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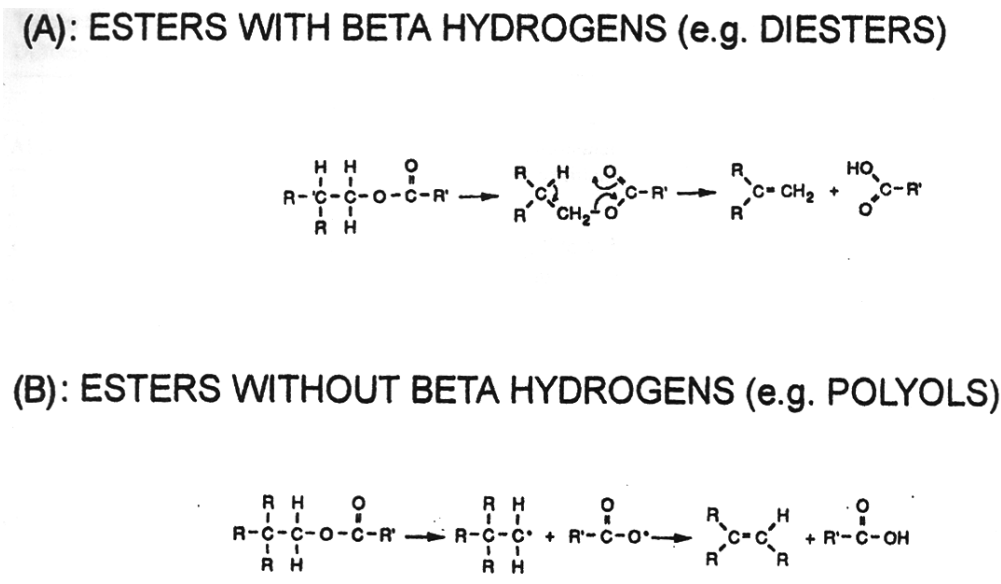

Figure 5 Thermal decomposition mechanisms for esters of two types.

chains. Therefore, as a general rule, linear alkyl esters tend to be more thermally stable than the branched variety. However, if the less stable tertiary hydrogens can be sterically hindered by adjoining methyl or ethyl groups, significant improvements in stability can be obtained [5].

The olefinic (C═C) bonds in the oleate chain of polyoleates make such molecules less stable to oxidation, especially at high temperatures. In several applications there is evidence of a direct link between the iodine number of the ester and sludge formation. Unfortunately, long chain molecules need to have some unsaturation for low temperature fluidity. It is important that the degree of unsaturation be minimized. It is especially important to avoid conjugated double bonds.

Aromatic molecules are very stable against oxidation. This stability is due to an energetically favorable atomic arrangement and a unique bonding system that make the molecules slow to break apart and participate in free radical reactions. When aromatic molecules do break down, they often form soft carbonaceous deposits that can actually aid in lubricity.

The foregoing trends are amply demonstrated in Figs. 6 and 7, which show differential scanning calorimetry and thermal gravimetric analysis, respectively, of several model wholly linear acid and wholly branched acid polyol esters. Note that once formulated, all the esters are at least as stable as mineral oil. PE linear esters are very thermally and oxidatively stable and for this reason are the lubricant of choice for military jet fighters.

Various additives can be used to improve the oxidative stability of ester lubricants, namely:

antioxidants (e.g., phenolics and amines), which act as free radical scavengers
antiwear additives (e.g., phosphites and phosphates), which can act as hydroperoxide scavengers and metal passivators, respectively
metal passivators (e.g., phosphates)
metal deactivators (e.g., thiadiazoles)

Mixtures of antioxidants, antiwear additives, and metal deactivators have been found to be synergistic. Additives, however, can markedly reduce the stability of an ester as well. Examples are as follows:

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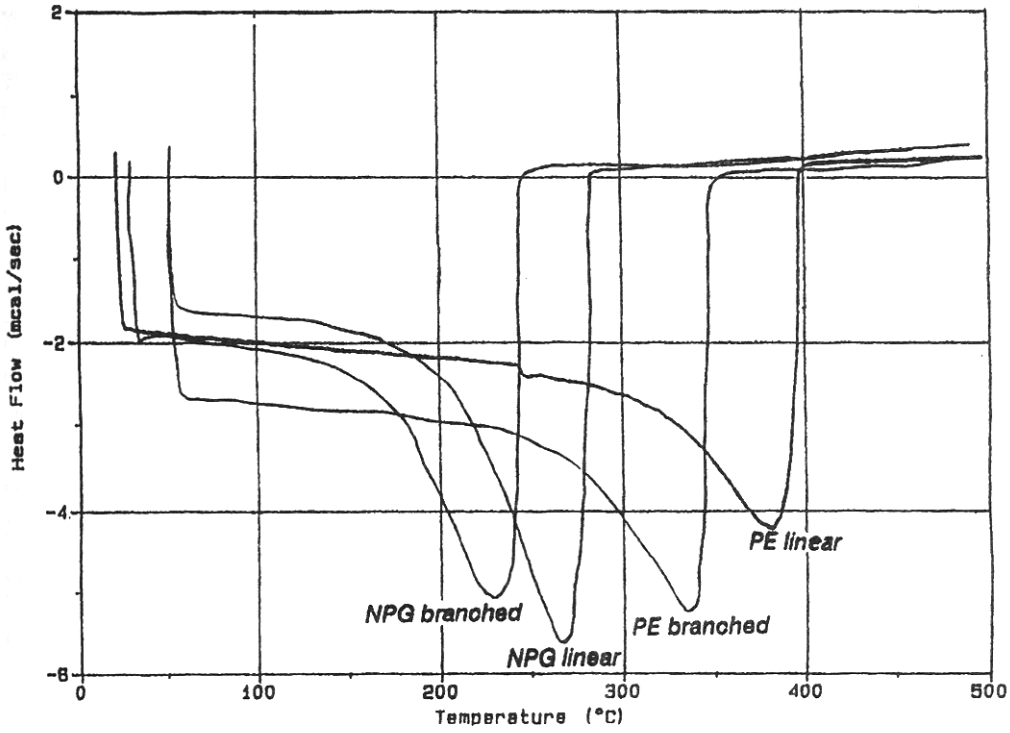

Figure 6 Differential scanning calorimetry on several POEs in nitrogen.

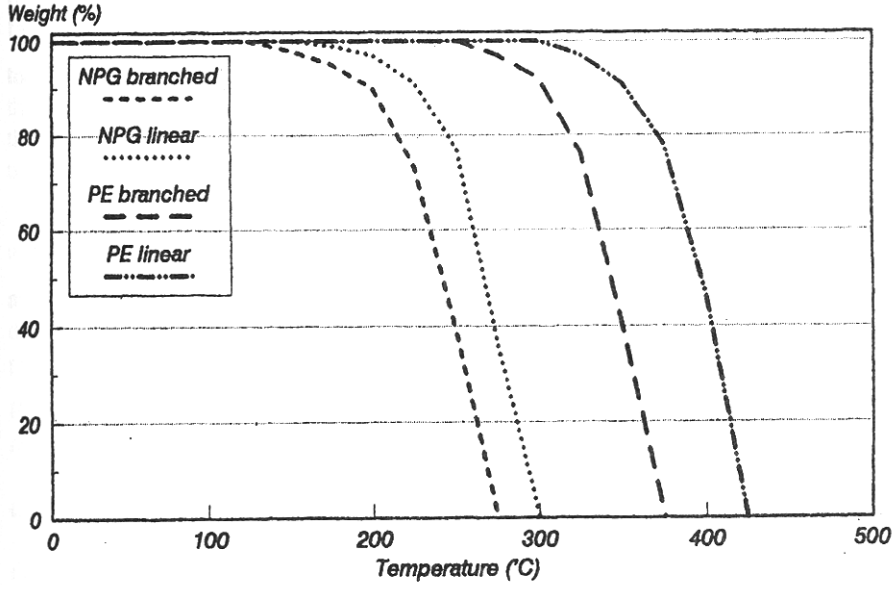

Figure 7 Differential thermogravimetric analysis on several POEs at 10°C/min in nitrogen.

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acidic additives (e.g., anticorrosion, antiwear), since high acidity tends to catalyze ester decomposition
metal deactivators, since at temperatures above 1308C certain metal deactivators form decomposition products that will destabilize the ester

The deposit-forming tendencies of lubricants depend on the following factors:

oxidative stability of the lubricant
polarity of the ester (which affects detergency and dispersancy)
process residuals
additives

The presence of air and metals can have a major effect on the deposit-forming properties of esters [6]. The deposit-forming tendencies of lubricants can be evaluated by the Panel Coker test. Here, the lubricant is dropped onto a steel plate at 2758C for 22 hours in air. The lubricant is collected at the bottom of the plate and recirculated for repeated application to the steel plate. At the end of the test the deposits are visually analyzed and given a demerit rating. Several lubricants to which 1% aminic antioxidant was added have been evaluated. These results can be seen in Table 11.

The results clearly show the effects described above. Aromatic phthalates give superior results to diesters. Esters that lack a β-hydrogen (polyols) are superior in performance to diesters. The excellent performance of the optimized esters shows what can be achieved.

The effect of process residuals (catalysts, neutralizing agents, etc.) can be seen in Table 12. It is clear that even small levels of certain contaminants can make a huge difference to the deposit-forming tendency of an ester. This reemphasizes the need for a tight specification.

As would be expected, additives can also have a major impact on the deposit-forming tendencies of an ester. As seen later (Table 16), when it comes to deposit formation for ester-based air compressor lubricant, additives are not always beneficial. Poor or incorrect selection of additives containing sulfur, sodium, or calcium can be particularly detrimental.

Esters made from linear acids generally have higher flash points than those made from

Table 11 Panel Coker Results on Various Lubricants plus Additive: 1% Aminic Antioxidant at 275°C for 22 hours, in Air

Candidate oil +1% aminic antioxidant	Visual demerit rating[a]
Mineral oil	3.95
PAO 6	>4.00
Diester	2.50
Phthalate	1.07
Trimellitate	0.50
Trimellitate[b]	0.04
TMP polyol ester	0.57
TMP polyol ester[b]	0.18

[a] Visual rating system: >2.0, fail; 0.5–2.0, pass; <0.5, excellent.
[b] Structure and process optimized to give low deposits.

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Table 12 The Effect of Process Residuals on Deposit Formation of a Trimelliate in the Panel Coker Test: 275°C for 22 hours in Air

Residual metals (ppm)	Visual demerit rating[a]
11–15	1.33
6–10	1.01
0–5	0.50

[a] Demerit rating system: >2, fail; 0.5–2, pass; <0.5, excellent.

branched chains or linear and branched chains. Increasing molecular weight also increase flash points. The volatility of esters depends on several factors:

Increasing molecular weight decreases volatility.
Increasing the degree of branching increases volatility.
Increasing polarity decreases volatility.
Oxidative stability (i.e., esters low in oxidative stability break down to form molecules of low molecular weight).

2. Hydrolytic Stability

The hydrolysis of an ester, that is, its cleavage into an alcohol and an acid, has been the subject of many discussions. Ester lubricants are required to be hydrolytically stable because they are often exposed to humid atmospheres during use, in addition to coming into contact with appreciable quantities of water. In practice, hydrolysis has proven to be a less serious problem than theoretical predictions would indicate. The hydrolytic stability of esters depends on several factors:

the molecular geometry of the ester used
the processing parameters of the ester
the additives used in the ester
the system it is used in

The final processing parameters of the ester need to be tightly controlled because they have a major impact on the hydrolytic stability of the product. These parameters are:

acid value
degree of esterification
process residues (e.g., catalyst, neutralizing agent, etc.)

Esters must have a low acid value, a very high degree of esterification, and a low level of process residues for the effects of molecular geometry to assert themselves.

Molecular geometry can affect hydrolytic stability in several ways. By sterically hindering the ester portion of the molecule, it is possible to retard hydrolysis. This is best achieved by sterically hindering the ester linkage of the acid portion of the ester. Conversely, hindrance of the alcohol has relatively little effect. To achieve steric hinderance, geminal dibranched acids (such as neoheptanoic acids) and 2-ethyl hexanoic acids have been used. However, there are penalties associated with the use of these feedstocks, namely, very long reaction times to achieve

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complete esterification. This of course translates into more expensive products. The polar substituent on the acid portion of the molecule have also been shown to have an effect on the hydrolytic stability of the ester. The hydrolytic stability of the polyols is generally regarded as superior to that of the diesters.

The first step in hydrolysis is cleavage at the ester linkage. As such, if the ester linkage can be hindered, hydrolysis will occur at a much slower rate. One obvious way of causing hindrance is to use a branched acid, especially those branched near the ester linkage (e.g., 2-ethylhexyl or neo-pentanoic acids). Branching will have an effect on the rate of hydrolysis, but ultimately the degree of hydrolysis will be determined by the total amount of water present; that is, given time, linear and branched esters will equilibrate to similar levels.

These effects are illustrated in Table 13. Several different types of ester were evaluated using an extended 2-week beverage bottle test. The aromatic phthalates and trimellitates are seen to be more stable than diesters. To obtain the same viscosity as the phthalate, a smaller alcohol must be used. A smaller branched alcohol causes less steric hindrance; hence the phthalate is more stable than a trimellitate of equal viscosity. The effects of steric hindrance on hydrolysis can again be seen if the linear PE polyol result is compared to the branched polyol. In this analysis, the branched polyol is found to be significantly more stable.

Acidic additives (e.g., certain anticorrosion and antiwear additives) can have a major negative effect on the stability of the ester. High levels of acidity can autocatalyze the breakdown of the ester (organic acids can act as a catalyst). Phosphate ester antiwear agents, such as tricresyl phosphate (TCP), are less hydrolytically stable than most esters. These additives can break down to produce acid, which can again autocatalyze the breakdown of the ester. Table 14 shows the major detrimental effect on the stability of linear and branched polyols of an acidic antiwear agent. When the excess acidity of additive is neutralized the decrease in stability is reduced. Table 14 also shows that other additives (e.g., acid catchers) can be used to markedly improve the stability of the ester.

3. Environmental Performance

Esters from Renewable Resources. Lubricants synthesized from renewable resources will become more and more important as a result of two main factors: the importance of life cycle analysis (LCA) calculations and cost.

In certain countries, tax incentives and grants are available to make the use of renewable resource materials a source of major potential cost savings.

Several acids used to make polyol esters (POEs) are available from renewable resources. Examples are as follows:

Table 13 Two-Week Beverage Bottle Hydrolytic Stability Test (ASTM D-2619) on Various Esters

Ester type	ISO grade	Viscosity change (cSt)	Initial acid value (mg KOH/g)	Acid value change (mg KOH/g)	Copper weight change (% loss)
Diester	46	−1.6	0.09	2.08	−0.01
Phthalate	46	+0.3	0.02	0.25	−0.03
Trimellitate	46	−1.2	0.04	0.43	−0.06
PE, linear	32	−0.7	0.05	1.93	−0.06
PE, branched	46	−0.6	0.06	0.19	0.00
TMP oleate	46	−1.7	2.00	14.02	−0.05

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Table 14 Effect of Branching and Additives on Hydrolytic Stability by the Two-Week Beverage Bottle test (ASTM D-2619)

Ester type[a]	Initial viscosity (cSt)	Viscosity change (cSt)	Initial acid value (mg KOH/g)	Change in acid value (mg KOH/g)
Linear PE				
PE alone	31.4	−0.7	0.02	1.90
PE + AW	31.2	−2.5	0.45	56.40
PE + AWN	31.4	−1.2	0.02	19.5
PE + AC	31.4	−0.4	0.02	0.01
Branched PE				
PE alone	45.1	−0.06	0.02	0.19
PE + AW	44.9	−0.4	0.47	0.55

[a] AW (antiwear) = acidic phosphate; AWN = neutralized AW; AC (acid catcher) = epoxide.

linear heptanoic acid from castor oil steam cracking
linear octanoic acid from coconut palm kernel oils
C6–C24 acids from natural oils
oleic acid from tallow oil

As biotechnology develops, it is inevitable that more and more raw materials used for ester production will come from renewable materials.

Biodegradability. The biochemistry of microbial attack on esters is well known in general outline and has been well reviewed [7–10]. The main steps are as follows:

ester hydrolysis
β-oxidation of long chain hydrocarbons
oxygenase attack on aromatic nuclei

The main features that slow or reduce microbial breakdown are as follows:

the position and degree of branching
the degree of saturation in the molecule
the presence of aromatic groups
high molecular weight

Table 15 gives biodegradabilities for a range of esters measured by two types of test. Generally, linear polyol esters tend to be used if high biodegradabilities are required. The biodegradability of esters is discussed in greater length in Chapter 34.

Toxicity and Ecotoxicity. Considerable environmental testing has been carried out on ester fluids. It is clear from this work that these substances are of a low order of toxicity.

Handling. In general, esters cause minimal acute toxicity by ingestion and skin absorption. Neither mineral oils nor esters show significant skin irritancy response. However, mineral oils have been known to cause skin problems in people who take inadequate precautions despite constant exposure. The solvency of the mineral oils can lead to the removal of some of the fat from the skin. After prolonged contact, such defatting can result in mild dermatitis. Esters are polar and therefore tend to be superior to mineral oil as solvents. There is potential, therefore,

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Table 15 Biodegradabilities of Various Esters

Ester type	Biodegradability	
	CEC L 33 A 93 (% in 21 days)	OECD 301B (% in 28 days)
Monoesters	70–100	30–90
Diesters	70–100	10–80
Phthalates	40–100	5–70
Trimellitates	0–70	0–40
Dimerates	20–80	10–50
Linear polyols	80–100	50–90
Branched polyols	0–40	0–40
Complex polyols	70–100	60–90

to give such responses more quickly. Where contact with esters is likely to be high, gloves should be worn [11].

Because of their hygroscopicity and their potential for hydrolysis, esters should be stored in dry sealed drums wherever possible, and contact with moist air should be minimized.

Recycling and Reuse. Energy recovery is the most common form of lubricant waste disposal. The major environmental issue when used esters are disposed of by incineration is the presence in the waste of other possible components/contaminants. Predominant among these concerns is contamination by polychlorobiphenyls (PCBs), halogens (especially chlorine), and metals. Many countries limit on the maximum total halocarbon, PCB and metal allowable in lubricants that may find their way into fuel supplements. No PCBs are present in the raw materials or production process used to synthesize esters, nor do esters decompose to form such products.

Waste ester is not a fuel in the strict technical sense because its volatility and viscosity are unlikely to conform to fuel oil standards. In conventional combustion plants, waste oil is burned in an admixture of lubricant to diesel fuel or coal in proportions that promote efficient combustion and allow the overall level of contamination to be controlled. Trials on the combustion of used ester oils in concentrations of 5–20% have been carried out [12]. In comparison with diesel oil, no differences were noted when such mixtures were burned, and all the emission readings were the same order of magnitude.

Used ester oils are currently being recycled and reused in the same applications as their original use in several areas (e.g., hydraulic, metalworking, and transformer fluids). Recycling trials on polyol ester using a thin film evaporator have shown great promise.

B. Physical Properties

1. Viscosity

The viscosity of ester lubricants can be increased by means of the following measures:

increasing the molecular weight of the molecule by (a) increasing the chain length of the acid, (b) increasing the chain length of the alcohol, (c) increasing the degree of polymerization, and (d) increasing the functionality of the ester.

increasing the size and/or the degree of branching
including cyclic groups in the molecular backbone
maximizing dipolar interactions
decreasing the flexibility of the molecule

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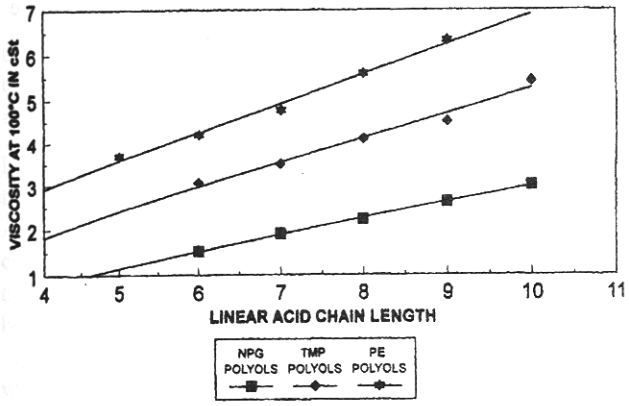

Figure 8 Effect of chain length on viscosity at 100°C for a range of linear acid polyol esters.

Figure 8 shows the change in viscosity at 1008C with acid chain length for a range of polyol esters. Branching can also have a marked effect on viscosity, as indicated by the following data:

Polyol ester	Viscosity at 100°C in (cSt)
PE linear octanoate	5.58
PE 2-ethyl hexanoate	6.36
PE isooctanotate	8.35

For very viscous molecules, branched aromatic esters or polymeric esters tend to be used. For low viscosity esters, short chain NPG polyols or monoesters are used.

2. Flow Properties

The viscosity index (VI) of an ester can be improved by the following means:

Increasing the acid chain length.
Increasing the alcohol chain length.
Increasing the linearity of the molecule. Branching restricts the rotational freedom around the ester linkage and also increases the ratio of length to cross section. Both effects contribute to lowering the VI.
Not using cyclic groups in the backbone, which tend to lower VI even more than aliphatic branches.
Molecular configuration. Viscosity indices of polyol esters tend to be somewhat lower than those of their diester analogues because the polyol molecule has a more compact configuration.

The pour point of the lubricant can be improved by several measures:

Increasing the amount of branching.
Fine-tuning the positioning of the branch. Branching in the center of the molecule gives better pour points than branches near the end.
Decreasing the acid chain length.
Decreasing the internal symmetry of the molecule.

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Esters made from mixtures of linear and branched chains have viscosity indices between those of linear and branched, but their pour points are lower than those of the esters used from either branched or linear chains.

Pour point depressants can also be used, but they tend to be much less effective in esters than in mineral oil.

Clearly, there is a trade-off between viscosity index and pour point: increasing the linearity of the ester improves the viscosity index improves, but the pour point deteriorates.

3. Lubricity

To understand how an ester lubricates, it is first important to understand its behavior in the different lubrication regimes.

Hydrodynamic Lubrication. The viscosity of a lubricant has a marked effect on wear (viscosity being related to film thickness). Viscosities of lubricating oils are often quoted at 408C (ISO grade) or 1008C. In reality, the viscosity under operating conditions is the controlling factor.

For systems experiencing hydrodynamic and elastohydrodynamic lubrication (EHL), the viscosity of the lubricant is a key requirement. The viscosity of the lubricant depends on several factors:

the viscosity at 408C
the temperature (which is related to the viscosity index)
the pressure (which is related to viscosity pressure coefficient)
the dilution of the lubricant by absorbed gases (which is related to vapor–liquid equilibrium, VLE)
the effect of shear rate on viscosity.

The viscosity of an ester at 408C can be modified by the factors discussed in Section III, B.I.

The viscosity index of the lubricant depends primarily on the degree of linearity and the length of the acid chain. Wholly linear acid polyol esters tend to have indices in the region of 110–130, while wholly branched POEs have viscosity indices in the region of 55–65.

Esters generally have poorer viscosity–pressure coefficients than mineral oil, but this disadvantage is somewhat offset by the esters superior VI and boundary lubricity. The pressure–viscosity coefficients of various lubricants have been measured at the following temperatures:

	Viscosity pressure coefficient (GPa^{-1})	
Type of oil	**40°C**	**80°C**
ISO 32 alkyl benzene	**30.2**	**22.0**
ISO 32 naphthenic mineral oil	**26.1**	**19.0**
ISO 32 PE polyol ester	**15.2**	**12.8**
ISO 68 PE polyol ester	**19.3**	**14.9**
ISO 68 trimellitate ester	**16.6**	**13.9**

These compare well with literature values at 408C [13–16] for TMP ester (8.4–9.8 GPa^{21}), PE esters (7.5–12.2 GPa^{21}), phthalates (13.6 GPa^{21}), and diesters (6.6–7.6 GPa^{21}).

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The viscosity pressure coefficient of a lubricant seems to be influenced by three properties:

the length of the side chains (the longer the better)
the degree of branching (the more the better)
aromaticity (the more the better)

Large, inflexible, unsymmetrical esters have large free volume and are much harder to pack together under pressure. This probably explains their superior viscosity–pressure coefficients. As the temperature increases, there is an increase in the free volume of the molecules, which causes, the pressure–viscosity coefficient to decrease, leading in turn to less interaction between the molecules. Inter- and intramolecular bonding will also play a role, but this area has not yet been sufficiently explored to warrant definitive comment.

Dissolved gases in the lubricant can seriously reduce the viscosity of lubricants and cause wear by removing protective lubricant films (e.g., on the cylinder walls in reciprocating compressors). For gases of certain types, synthetics are much better at resisting this dilution effect. This area is discussed at greater length in Chapter 25 on refrigeration lubricants.

Elastohydrodynamic Lubrication (EHL). As the lubrication regime passes from hydrodynamic into EHL, the materials of construction become more and more important. EHL films are thin and require smooth surfaces to prevent contact with asperities. The hardness and surface treatment of materials used is therefore important. As the contact pressures increase, the viscosity–pressure coefficient of the lubricant will become increasingly important.

The polarity of the ester can also be very important. Recent work suggests that when a small amount of a high viscosity polar ester is added to a low viscosity nonpolar base fluid (PAO), the ester will preferentially stick to the surface. When the two metal surfaces are far apart, the bulk viscosity is controlled by the PAO. When the surfaces come closer together, the PAO is squeezed out of the contact zone. The polar ester sticks to the surface and stays in the contact area. Since the ester has high viscosity, the bulk viscosity of the oil will increase as the surfaces come closer together. Finally, a point will be reached at which only the more viscous polar ester remains. This is depicted schematically in Fig. 9 [17].

Mixed Film. Mixed film lubrication, as the term implies, is actually a combination of boundary, hydrodynamic, and EHL regimes. In the mixed lubrication regime the contact characteristics are determined by varying combinations of fluid film and boundary lubrication effects. Some asperity contact may occur, and interaction takes place between mono- and multilayer boundary lubricating films, while a partial fluid–film lubrication action develops in the bulk of the space between the metal surfaces. It follows that both the physical properties of the lubricant (as with EHL) and the chemical properties of the lubricant (as with boundary) are important.

Boundary Lubrication. The properties of the bulk lubricant (e.g., viscosity) are of minor importance in boundary lubrication. The surface phenomena that determine the behavior of boundary lubricants can be described in the following terms:

physically absorbed layers of gas, liquid, or solid lubricants
chemically absorbed layers
films formed by chemical reaction

Esters have a high degree of polarity owing to the lone pair of electrons on the oxygen atom of the ester linkage. Polar molecules are very effective boundary lubricants because they tend to form physical bonds with metal surfaces (i.e., they stick to the surface better than mineral oil). Most metal oxide surfaces are partially hydroxylated in the presence of water vapor. This hydroxylated surface can participate in hydrogen bonding as either a donor or an acceptor of

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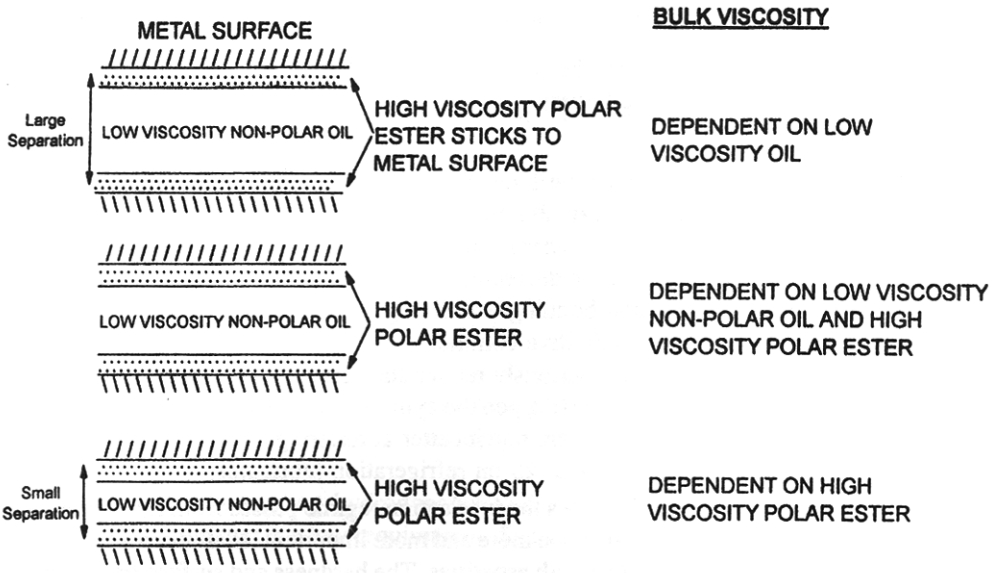
METAL SURFACE
BULK VISCOSITY
Large Separation
LOW VISCOSITY NON-POLAR OIL
HIGH VISCOSITY POLAR ESTER STICKS TO METAL SURFACE
DEPENDENT ON LOW VISCOSITY OIL
LOW VISCOSITY NON-POLAR OIL
HIGH VISCOSITY POLAR ESTER
DEPENDENT ON LOW VISCOSITY NON-POLAR OIL AND HIGH VISCOSITY POLAR ESTER
Small Separation
LOW VISCOSITY NON-POLAR OIL
HIGH VISCOSITY POLAR ESTER
DEPENDENT ON HIGH VISCOSITY POLAR ESTER

Figure 9 High viscosity esters as boundary lubricants.

hydrogen atoms. Thus, absorption of hydrogen atom acceptors such as ester lubricants (or decomposition by-products such as alcohols and carboxylic acids) leads to wear protection and friction reduction [18]. Esters therefore tend to be more effective lubricants than nonpolar mineral oils. Hydrogen bonds tend to be quite weak, and as loads and temperature increase they will break down. However, at higher loads esters will tend to form chemisorbed films.

Chemisorbed films are produced by the formation of soaps. Soaps tend to act as friction modifiers. The effectiveness of these films is limited by the melting point of the soap. For many metal soaps, the melting point is in the range of 120–2008C, and when this point is reached, they desorb and the boundary lubricating properties are lost. Under extreme boundary conditions esters tend to break down to form acids. Preliminary work suggests that these acids further react to form soaps and metal carboxylates. Metal carboxylates have been shown to convey good extreme pressure (EP) protection.

A form of boundary lubrication can be given at higher temperatures by the incorporation of EP or load-carrying (antiwear) agents. Sulfur, for instance, will start to react at about 1008C to form sulfides with melting points in excess of 10008C. It is worth noting that oxygen from the atmosphere, or free oxygen in the lubricant, is a valuable EP lubricant. The oxide layers that form generally provide a low shear strength film capable of reducing friction and wear between bearing materials. Mineral oil contains small but important quantities of more reactive substances like sulfur, nitrogen, and oxygen. These chemicals readily react with newly exposed metal surfaces to provide boundary lubrication.

Because of these different interactions, the lubricity of an ester in a fully formulated fluid is not always easy to predict. Since ester groups are polar, they can compete with antiwear or EP agents for the metal surface.

When a very polar base fluid is used, it can cover the metal surfaces instead of the antiwear additives, resulting in higher wear characteristics. This is because, although esters are superior to mineral oil in lubricity properties, under high load conditions they are certainly less efficient than antiwear additives. It is therefore very important to choose the correct additive and to

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optimize its concentration to get the full lubricity benefit of using ester base stocks. Often, operators offset this factor by using more polar antiwear agents or the same antiwear agent at a higher dose rate. Alternatively, the ester can be modified to decrease its polarity.

Esters can be classified in terms of their polarity, or nonpolarity, by means of the following formula [19]:

$$\text{Nonpolarity index (NPI)} = \frac{\text{Total no. C Atoms} \times \text{RMM}}{\text{no. of carboxylate groups} \times 100}$$

where RMM 5 relative molecular mass.

Generally, the higher the NPI the lower the affinity for the metal surface. Esters with high NPI will therefore compete less with the antiwear package.

Figure 10 is a graph that plots wear (as evaluated by the four-ball test) versus nonpolarity index. As a general rule, increasing molecular weight improves overall lubricity. The scatter is large because the formula takes no account of the configurational aspects of the lubricant (i.e., whether it is branched or linear).

As viscosity is reduced, or if shear rate or load is increased, the chance of boundary lubrication occurring increases. This is especially true under conditions of compressor start-up, where the lubricant film may not yet have formed. The following properties of the lubricant affect boundary lubrication:

degree of branching
molecular weight
polarity
additives present in the lubricant

Figure 11 shows a simplistic model of a monoester on a metal surface. As the acid chain length increases, the film thickness of the lubricant increases. Linear chains also increase the degree an ester can pack together on the metal surface. As discussed in Section III. B. 1, branched chains give a higher viscosity than linear ones of the same length. Therefore, for a given ISO grade, linear esters will have a longer chain and therefore potentially a thicker film. For diesters the length of the diacid used to make the ester is very important. Longer chain diacids produce an ester with a greater distance between the two carboxylate linkages. This makes them less polar and therefore reduces their affinity for metal surfaces. This property, a disadvantage in

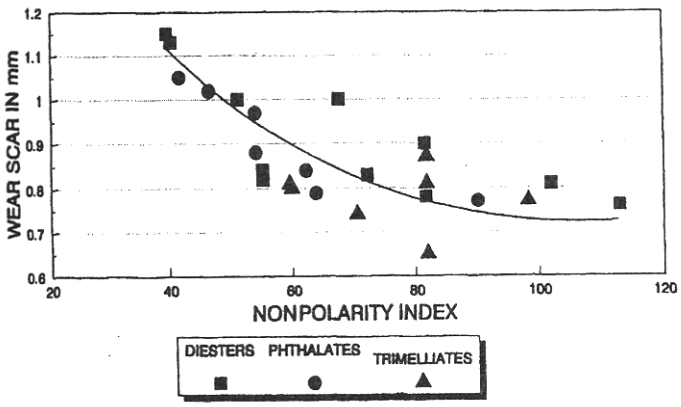

Figure 10 Four-ball, one wear scar, versus nonpolarity index for a range of esters.

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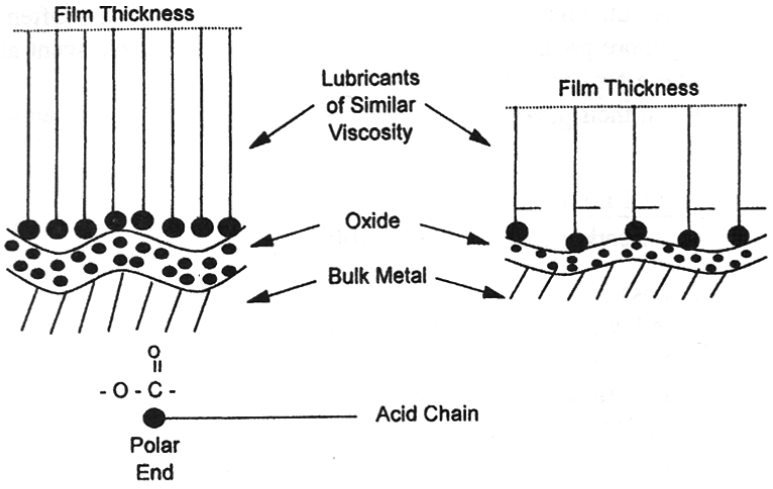

Figure 11 Boundary lubrication schematic: effect of ester structure.

unformulated lubricants, can be advantageous in a formulated lubricant, since the less polar compound allows the antiwear package easier access to the metal surface.

Surface force apparatus experiments on linear and branched alkanes have shown that even a small amount a branching (a methyl side chain) can significantly reduce the ability of molecules to form discrete layers between solid surfaces [20].

The use of bench tests (e.g., four-ball, Falex) is an attractive approach to wear testing. Their low cost, short duration, and ease of operation make them a desirable research tool. Despite justifiable reluctance to rely on lubricant performance data obtained from the use of bench wear tests, these assays are useful as an initial screening tool to spot crude trends that can later be checked by system trials.

Figure 12 plots 1-hour, four-ball wear scars (steel/steel) for a range of wholly linear or wholly branched polyol esters against viscosity at 508C (bulk oil temperature). Opposite trends are seen for linear versus branched POEs, with linear esters giving the lower wear for a given

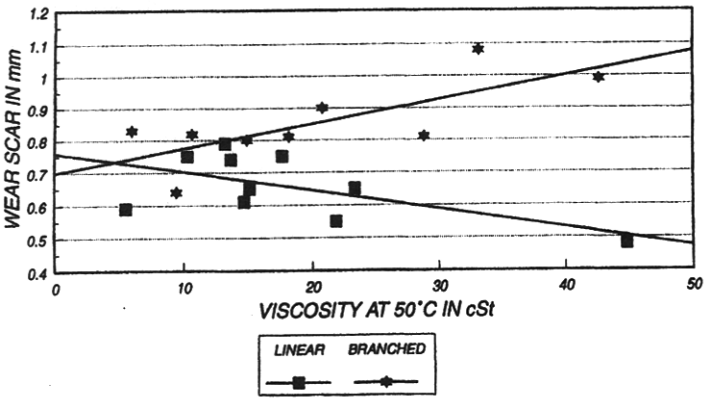

Figure 12 Four-ball wear scar versus viscosity at 50°C for a range of wholly linear or branched acid chain polyols.

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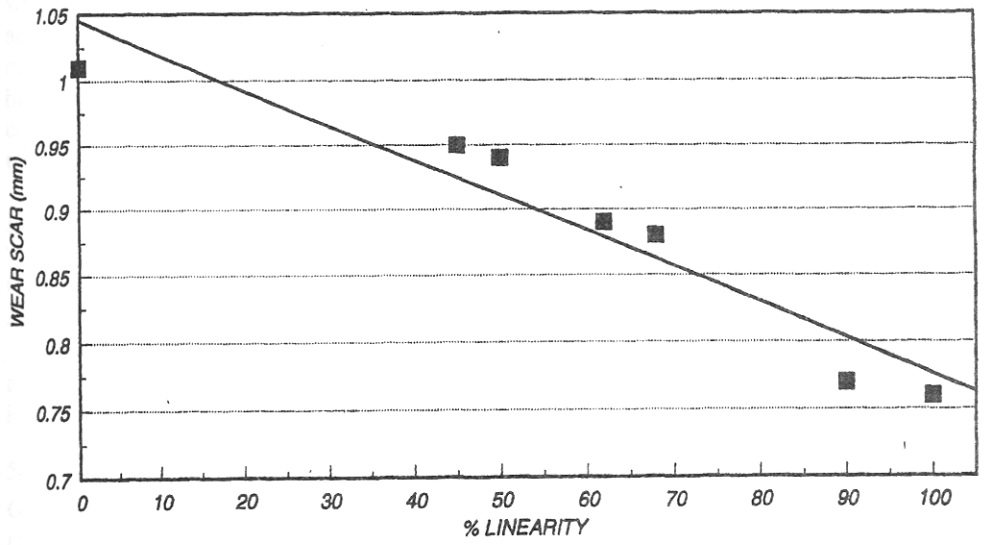

Figure 13 Effect of linearity on the wear performance of ISO 32 polyols as measured by the extended four-ball test (steel/steel, 30 kg, for 2 h).

viscosity. The trend is not, as the graph implies, totally viscosity dependent. The viscosity of the POEs is very dependent on acid chain length, and it is this parameter that is the key factor.

Figure 13 uses a 2-hour, four-ball test to look at range of ISO 32 pentaerythritol polyol esters. To maintain viscosity as the degree of branching is increased, the chain length must be decreased. Again, a strong relationship is seen between the degree of linearity and wear performance. Figure 14 continues this analysis by comparing the degree of linearity versus Falex load to fail for several polyol esters.

If wear is still a problem after the structure of the lubricant has been optimized, a change of materials at the wear contacts could be considered. The following material modifications are possible:

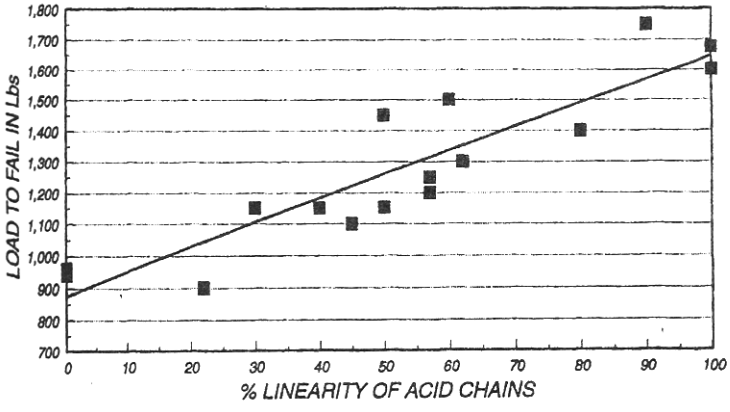

Figure 14 Falex load to failure (steel/steel) versus percentage linearity of acid chains for a variety of polyol esters.

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changes in the hardness of material
modifications to the shape of contacts (e.g., vane tips in rotary compressors)
surface treatment (e.g., phosphating and SiN coatings)
modifications to improve flow of lubricant to wear surfaces

To summarize, if wear using an ester is seen, several methods can be used to reduce it, namely:

Increase the viscosity of the lubricant.
Improve the flow of lubricant to the wear surface.
Modify the chemistry of the lubricant (more linear).
Modify materials of construction (harder).
Modify assembly tolerances.
Use antiwear/EP additives.

4. Energy Efficiency

Federally mandated requirements for higher energy efficiency refrigeration compressors are being introduced in the United States. Improvements in gasoline consumption requirements are also required in the automotive sector. Legislation in this area is likely to tighten and spread to other application areas.

A lubricant can affect the energy efficiency of a system in various ways, namely:

viscosity (lower viscosity lubricants reduce viscous drag)
frictional effects of (a) the lubricant, (b) any additives, and (c) the materials of construction
volumetric efficiency
heat transfer properties

Lower viscosity lubricants improve energy efficiency by reducing losses due to viscous drag. In compressor applications that call for moving from a mineral oil to an ester lubricant, the increased lubricity and flow properties of the ester can allow a decrease in the bulk viscosity of the ester lubricant compared to that required for mineral oil.

Esters have much lower coefficients of friction than mineral oil. Figure 15 shows that as

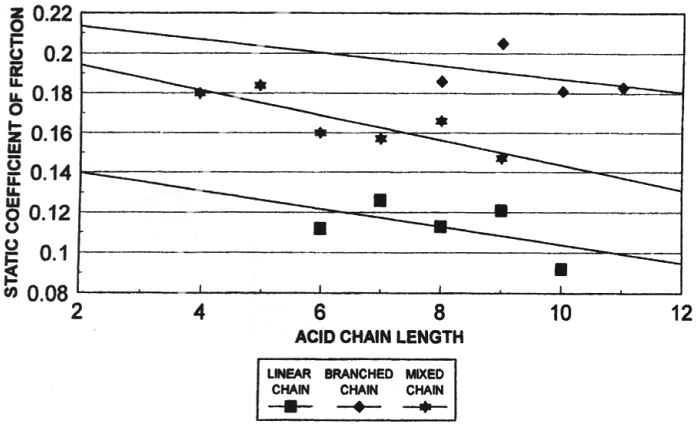

Figure 15 Static coefficients of friction versus chain length for a range of TMP polyol esters.

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with wear, polar long linear alkyl chains give the lowest coefficients of friction [21]. Esters can act as friction modifiers: even when the ester is added at only 5% w/w, the coefficient of friction of the lubricant formulation can be significantly reduced [22]. Certain types of antiwear additive have been shown to reduce friction. Friction-modifying agents such as PTFE and molybdenum compounds are also very effective at reducing friction at surface contacts. As with antiwear agents, esters may compete with friction modifiers at metal surfaces.

Volumetric efficiency is a very important factor in the energy efficiency of compressors. If the viscosity of the lubricant is reduced to an excessively low level, piston blowby occurs. This results in poor energy efficiency. Excessive foaming can also reduce volumetric efficiency. On the downstroke of the piston, the foamy layer is compacted. This compaction absorbs energy and can thereby further reduce energy efficiency.

In refrigeration and heat pump applications, the lubricant can coat out on the heat exchanger and thereby reduce heat transfer, exerting a major impact on energy efficiency. This is discussed in more detail in Chapter 25.

5. Solvency

Compatibility with Additives and Other Lubricants. Generally, esters are fully compatible with mineral oils. This gives them several major advantages:

There are no contamination problems: esters can be used in machinery that previously used mineral oil.
Most additive technology is based on mineral oil, and it is therefore usually directly applicable to esters.
Esters can be blended with mineral oil or natural oils (semisynthetics) to boost their performance.
Esters can be blended with other synthetics such as poly (α-olefins). This gives esters great flexibility and unrivaled opportunities to balance the cost of different lubricant blends against performance.

Since PAOs are low in polarity, solubility problems can often result from the use of additives containing these polymers. This is especially true for viscosity index improvers (VII).

In many applications esters are blended with PAOs to overcome these solubility problems. As the following sections show, ester/PAO blends can also offer advantages in other areas as well.

Elastomer Compatibility. Elastomers that are brought into contact with liquid lubricants will interact with the liquid that is diffusing through the polymer network. There are two possible kinds of interaction: chemical and physical.

Chemical interactions of elastomers with esters are rare. During a physical interaction of an ester lubricant and an elastomer, two different processes occur:

an absorption of the lubricant by the elastomer causing swelling
an extraction of soluble components from the elastomer, causing shrinkage

The degree of swelling of elastomeric material can depend on the following factors:

Molecular size of the lubricant component. Generally, the larger the lubricant, the smaller the swelling.
The closeness of the solubility parameters of the lubricant and the elastomer. Generally, the "like-dissolves-like" rule is obeyed.
The molecular dynamics of the lubricant. Linear molecules that contain flexible linkages allowing rotation can diffuse into elastomers more easily than branched or cyclic ones.

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Table 16 Guidelines on the Compatability of Elastomers and Plastics with Esters

Compatible	Not compatible
Viton	PVC
Teflon	Polystyrene and styrene (ABS)
Nylon	SBR Rubber
High nitrile (>33%)	Low nitrile (<33%)
Fluorosilicone	Neoprene
Polysulfide	Ethylene propylene copolymers, natural rubber, BUNA-s

The polarity of the lubricant. It is known that several elastomers are sensitive to polar lubricants.

The nonpolarity index can be used to model seal-swelling trends for specific ester types.

Several polar esters are well-known plasticizers used by industry. Nonpolar base stocks, such as PAOs, have a tendency to shrink and harden elastomers. A slight degree of swelling by elastomers is usually required for them to operate satisfactorily as seals. By means of carefully blending PAOs and esters, lubricants can be formulated to give good elastomeric performance. Table 16 gives an overview of the suitability of elastomers.

It is important to note that the processing of the elastomer can have a major impact on its performance. Esters, which can be efficient solvents, have the potential to extract any substances used during the manufacture of the elastomer. Elastomers from different suppliers can be highly different in terms of the degree of cross-linking agents, fillers, and process residuals in the elastomer. Therefore, any information on ester compatibility with elastomers in general should be confirmed by tests on the specific materials.

C. Application Areas

1. Engine Oils

Esters commonly used are diesters and polyols. Others include dimerates, polymeric esters, monoesters, and phthalates. Extended drain, as well as requirements for lower exhaust emissions and fuel economy, are market drivers.

During the last 10 years, several general trends have been seen in the automotive area:

requirements for improved fuel economy
cleaner exhaust emissions
harder working engines
extended drain intervals, to reduce maintenance times
increased use of turbochargers, air conditioners, engine management systems, etc.
longer engine life

Maximum engine torques have increased, compression ratios have been reduced, airflow around the engine has been reduced (owing to improved aerodynamics), and the increased use of auto air conditioners and other "under the hood" equipment has resulted in a significant increase in the demands made on the engine oil.

Low temperature viscosity is perhaps the single most important technical feature of a modern crankcase lubricant. Cold starts are a prime cause of engine wear, which can be mitigated only by the use of products providing immediately effective lubrication circulation. Low temperature viscosity can also have the benefit of reducing start-up load and stresses, reducing battery current drain, and making starting easier [23].

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To meet the new energy efficiency requirements, oils are moving to lower viscosity specifications (5W and 0W). The use of lower viscosity oils, which tend to be more volatile, has created the need to move increasingly toward synthetics. Low volatility is especially important in the context of the modern trend toward smaller sump capacities and longer oil-change intervals.

For both gasoline and diesel vehicles, electronic management systems have emerged and are part of all advanced engine designs. It is essential that sensors used in these systems not be subjected to deterioration due to lubricant breakdown.

The superior thermal stability of esters allows the use of low viscosity oils while at the same time offering the benefits of low deposits (extended drain time, cleaner systems) and low temperature fluidity (reduced wear on engine start-up). As the requirements placed on the engine oil increase, there is a growing trend to higher synthetic contents in engine oils.

It is now widely accepted that synthetic fluids, such as PAO/ester blends, offer a number of inherent performance advantages over conventional petroleum-based oils for the formulation of modern automotive engine oils. Practical benefits that may derive from their use include improved cold starting, better fuel and oil economy, plus improved engine cleanliness, wear protection, and viscosity retention during service. Fluid types used in the development of automotive crankcase oil, either commercialized or considered for commercialization, include PAOs, hydrocracked oils, diesters, alkylated aromatic hydrocarbons, and polyalkylene glycols. Experience from numerous laboratory engine bench and vehicle test programs conducted over the last 10 years has shown that an ester/PAO blend provides an excellent base fluid for the formulation of synthetic engine oils [24,25].

Initially formulators used PAO with a small amount of a phthalate, to act as a seal swellant, PAO/adipate ester blends were then used, with the diester at between 5 and 20%. Here, the ester acted as seal swellant and additive solubilizer and helped to achieve deposit/volatility targets. Adipates can also be used with mineral oil to produce semisynthetics. With the increased needs for superior thermal stability, TMP esters have substituted for adipate esters. For reasons of cost, hydrocracked oils are increasingly being substituted for the PAO. Certain hydrocracked oils are biodegradable and, when combined with ester, offer the opportunity of formulating biodegradable engine oils. However, there are potential problems with marketing such a product. In particular customer education is required to ensure that consumers realize that biodegradable engine oils cannot be poured down the drain but must be recycled.

Monoesters, such as glycerol monooleate, have been added by certain formulators at 0.5% to act as friction modifiers in diesel engine oils.

2. Two-Stroke Oils

Esters commonly used in two-stroke oils are dimerates and polyols.

Other esters include trimellitates and complex esters. The market for these products is driven by the desire for low smoke, improved engine cleanliness, and biodegradability.

Ester lubricants offer a number of advantages over mineral oils as the lubricant component of two-stroke engine mixtures. The clean-burn characteristics result in less engine fouling, with much reduced ring stick and lower levels of dirt buildup on ring grooves, skirts, and undercrowns. Ignition performance and plug life are also enhanced. Because the presence of polar ester groups in the molecule imparts increased adhesiveness to metal surfaces, esters have much better lubricity than hydrocarbons. This removes the need to use brightstock and simultaneously permits the use of leaner burn ratios. In turn, these advantages significantly reduce smoke levels. About 95% of the particulates in the exhaust fumes have been found to be from the unburnt lubricant [26]. A 25% decrease in the amount of polyaromatic hydrocarbons (PAHs) in the exhaust emissions of a two-stroke engine also was found when a carboxylic ester was used

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instead of mineral oil [27]. The PAHs have been found to be one of the major contributors to the carcinogenicity of exhaust emissions. The excellent solubility of esters also allows them to be used without solvents (which are usually added to conventional two-stroke oil to help miscibility with the fuel and low temperature fluidity).

The leaner burn ratios result in reduced oil emissions, which is a benefit in environmentally sensitive applications such as marine outboard engines and chain-saw motors. The high biodegradabilities of esters and the low ecotoxicity and clean-burn characteristics of ester formulations make them excellent candidates for "environmentally considerate" labeling such as Blue Angel in Germany. Where biodegradability is an important factor, TMP oleates have replaced dimerates.

Low temperature performance is important in some applications, such as engines used to power snowmobile-type vehicles. Therefore, esters with low pour points (∃ 2568C) are very suitable for fuels in these applications.

3. Compressor Oils

Esters commonly used in compressor oils are diesters, polyols, phthalates, and trimellitates. Other esters include complex esters. Properties identified as market drivers are extended drain, energy efficiency, biodegradability, and fire resistance.

This application area covers a wide range of compressor types, used for a number of different gases. The three basic functions of a compressor oil are to lubricate (reducing friction between moving parts), to act as an oil seal at rings, vanes, or rotary screws, and to cool critical bearings and points of constant friction.

Esters have several advantages in compressor applications. First, compressors that use esters can be less expensive to run. Such compressors also have safety and ecological benefits and are excellent lubricants.

From the user's standpoint, saving money is the main reason for choosing a synthetic over conventional hydrocarbons. This goal can be accomplished in part through extended drain intervals (up to eight- or tenfold) and other associated cost savings, such as less frequent replacements of oil filters and air/oil separators. Esters can have better lubricity, which can mean reduced wear and longer periods between replacements of mechanical parts such as piston rings, seals, and bearings. Another factor is power cost saving, which can range from 1 to 7% [28–30].

Resistance to breakdown means less sludge and varnish in the compressor and compressed gas system. There is also improved performance of newer compressors operating at higher speeds, temperatures, and pressures. From a safety performance standpoint there are reduced fire and explosion hazards for compressors handling air and chemical gasses. High outlet temperatures in modern reciprocating air compressor installations cause carbon buildup on compressor outlet/discharge valves. These carbon deposits can glow and cause fires and/or in some cases explosions. This problem is intensified in environments where air filtration is less than ideal and dust contributes to a buildup of dangerous deposits. Esters, especially trimellitates and polyol esters, have improved oxidation resistance and low volatility compared to those of mineral oils of similar viscosity. Esters therefore minimize buildup of deposits on hot pistons and discharge valves. Thus the high temperature stability and solvency action of esters minimize the risks of fire and explosion [30].

The low volatility of esters results in reduced carry over. These properties, coupled with their higher flash and autoignition temperatures, and the low order of toxicity for vapor inhalation and ingestion, make them considerably safer lubricants than mineral oil. Their low ecotoxicity and high biodegradability can also lessen their environmental impact.

The excellent lubricity, thermal stability, and conductivity of esters allow them to be used

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in high performance compressor oils that cannot be formulated using traditional hydrocarbon lubricants. Diesters and phthalates have found their major application in air compressor lubricants, but they are also used in compressors handling natural gas, propane, isobutane, and carbon dioxide. Diesters generally have higher viscosity indices, giving them a wide temperature range without the use of viscosity index improvers, which can shear in this application.

In reciprocating compressors, where significantly higher viscosity oils are preferred, trimellitates can be used. The solvency characteristics of esters are such that care must be taken in the selection of elastomeric sealing materials: the use of Viton is usually recommended. Diesters and polyol esters can also be blended with PAOs and/or hydrocracked oils for use in compressors of various types.

For the past 50 years, lubricants produced from naphthenic and paraffinic mineral oils have been used in refrigerator compressor systems. These oils were fully compatible with the traditional chloro-fluorocarbon (CFC) refrigerants (e.g., R12) and fully met system requirements. Because of chemical differences between CFCs and the new alternative refrigerants (e.g., R134a), traditional mineral oils are not capable of meeting these requirements. Ester lubricants based on polyol ester chemistry have been developed that achieve the key characteristics of this application, namely [31]:

good lubricity
good materials compatibility
good energy efficiency
good resistance to copper plating
good chemical, thermal, and hydrolytic stability
good solubility with R134a, mineral oil, and additives

4. Aviation Lubricants

Polyol esters are commonly used in aviation lubricants, although diesters are used, as well. Market drivers are improved thermal stability and reduced volatility.

The bulk of aviation lubricant demand is for gas turbine lubricants for both military and civilian use. The requirements placed on the jet engine lubricant in terms of thermal stresses cannot be met by hydrocarbon oils.

The first generation of oils (type 1) were diesters, but over the last 25 years these have slowly lost ground to the more expensive but more thermally stable type 2 and type 3 polyol esters. Some diesters are still used in less demanding applications such as small private aircraft or turboprop engines.

Type 2 aviation gas turbine lubricants are produced to a viscosity of 5 cSt (at 1008C). For some military applications, where operability at low temperatures is vital, the corresponding viscosity is reduced to 3 cSt. Type 3 oils are available at 4 and 5 cSt at 1008C. With increasing jet engine capabilities, the need for more thermally stable oils has increased. Maximum operating temperatures has now moved from 1758C to 2008C.

The additive package usually consists of an antiwear agent (e.g., TCP) and an aminic antioxidant. There has been some concern over the potential reaction of TMP polyols and TCP to form TMP-P, a potent neurotoxin [32,33].

5. Hydraulic Fluids

Monoesters, diesters, and polyols are commonly used in hydraulic fluids; other esters include PAG esters and complex esters. Market drivers are biodegradability, recyclability, and low and high temperature performance.

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Ester-based hydraulic fluids have achieved significant success in Western Europe, although use in the United States has been slow to develop. Ester base fluids are attractive because they:

are environmentally considerate
have reasonable level of fire resistance
have good high and low temperature flow properties
have good thermal stability
exhibit good wear performance

The low ecotoxicity and high biodegradability of esters permit them to obtain environmentally considerate "eco-label" status such as Blue Angel in Germany. This is a very important aspect, given estimates of leakage into the environment of 4% of hydraulic fluids, which in 1990 accounted for some 6000 tons in West Germany alone.

Several European countries have developed financial recompense schemes to encourage the use of natural oils (e.g., rapeseed) in industrial applications. The low price, low toxicity, and high biodegradability of natural oils make them interesting candidates for hydraulic fluids. Their poor oxidative stability and low temperature flow properties are major drawbacks, however. The oxidative stability of the natural oils can be improved by decreasing the degree of unsaturation, but unfortunately this makes their low temperature flow properties even worse. Biodegradable diesters and polyols blended with natural oil at between 5 and 20% in the presence of a pour point depressant have been found to improve the low temperature performance of these oils enough to make them eligible for use in countries such as Sweden and Norway.

Diesters blended with PAOs have been used as fire-resistant hydraulic fluids (MIL-H-83288C spec). However, polyol esters now tend to be used: normally esters of oleic acid, and most commonly the TMP ester of this acid. Polyol esters are classified as HFD U fluids. There are increasing concerns about the toxicity aspects around phosphate esters and the highly noxious nature of their thermal decomposition products. Polyol esters are therefore beginning to replace phosphate esters in certain areas. Polyols have several advantages over phosphate esters:

They are more cost effective.
They have better flow properties.
They are easier to recover from water.
They are less aggressive to seals.
They are better lubricants.

Phosphate esters, however, are superior in their fire resistance. To enable polyol esters to pass certain fire resistance tests (e.g., the factory spray test), , 0.5% of a viscosity index improver may be added. This additive helps modify the spray pattern of the fluid pumped through the nozzle by increasing the droplet size. Larger droplets of lubricant are much more difficult to ignite. Esters (e.g., isooctyl oleate) are also used in HFA SE (synthetic emulsion) fire-resistant fluids as well.

6. High Temperature Chain Oils

Esters commonly used: Diesters and polyols are commonly used in high temperature chain oils; trimellitates are used, as well. Market drivers are higher thermal stability and lower deposits.

Many manufacturing products today require extreme heat in the manufacturing, finishing, curing, or drying process. Textile factories, car plants, and pottery/glass kilns use roller chains, stenter chains, and sliding chains. Lubricants for these chains see temperatures above 1508C, and sometimes as high as a 10008C [34]. Below temperatures of 2008C, diesters are used; for temperatures between 200 and 3008C, polyol esters and trimellitates are used.

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7. Automotive Gear Oils

Esters commonly used in automotive gear oils are diesters and polyols. Here the market is driven by extended drain and fuel efficiency considerations.

Over the last 10 years the following trends in gear oils have been seen:

increased requirements for oxidatively stable oils
tightening of environmental legislation
improved shift feel

More oxidatively stable oils are required for several reasons. These are:

Increased aerodynamic styling, driven by the need to improve fuel efficiency. New designs lead to reduced airflow and therefore decreased cooling around the transmission, transaxle, and rear axle.
Logistics simplification, resulting in the reduction of components used in car production. This can lead to the use of the same transmissions and rear axles being used in both low and high powered cars.
Extended drain intervals to reduce maintenance times.
Installation of turbochargers, air conditioners, and catalytic converters, which has led to an increase in "under the hood" temperatures.

As with engine oils, good trade-offs in properties have been obtained with PAO/diester or PAO/polyol ester blends. As temperature requirements increase, polyol esters will increasingly be substituted for diesters.

The two main environmental issues are the handling and disposal of lubricants and fuel efficiency.

In Europe, a great deal of activity relates to the chlorine content of lubricating oils. The main concern is the potential formations of polychlorinated bipenyls (PCBs) and chlorinated dioxins during the re-refining process. In the United States, potential future increases in Corporate Average Fuel Economy (CAFE) standards are driving fuel efficiency requirements. Ester-based lubricant have given 0.5–6% improvements in gearbox efficiency [35,36].

8. Drilling Mud Lubricants

Monoesters are commonly used as drilling mud lubricants. Diesters also serve in this capacity. Market drivers are biodegradability, low ecotoxicity, good low temperature performance, and drilling speed.

Historically, either water-based muds (WBMs) or oil-based muds (OBMs) have been used for offshore wells. WBMs are widely used in shallow wells and often in shallower portions of deeper wells but are not effective in deeper wells and extended-reach wells. Drilling with WBMs often takes much longer than with OBMs, resulting in extra cost and air emissions from the drilling equipment.

Synthetic-based muds (SBMs) offer several operational advantages over WBMs and pollution prevention potential over OBMs in many situations [37]. An average North Sea well may generate approximately 1100 tons of cuttings which, prior to their restriction by legislation, contained roughly 15% by weight of oil. Therefore, 165 tons of an oil was being introduced into the environment from each well that was drilled using OBM [38]. It has been estimated that some 12,250 tons of oil was discharged into the North Sea during 1989 [39]. As a direct result of the large number of wells being drilled in the North Sea, governments introduced environmental restrictions to limit oily discharges.

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Ester-based drilling muds (EBMs) offer several advantages:

They are readily biodegradable.
They have low ecotoxity.
They can be made from renewable resources.
They are good lubricants.

Long chain monoesters and short chain diesters are in current commercial use.

9. Additive Carriers

Commonly used as additive carriers are the diesters. Phthalates and polyol esters are also used, however. The market for these products is driven by environmental factors.

As remarked earlier, esters make potentially good solvents. When this property is combined with their clean burn, biodegradability, and low toxicity characteristics, their usefulness as carriers of other chemicals or additives becomes transparent.

The increasing use of additives (e.g., detergents) in engine fuels has created the need for a carrier fluids that have good solvency, low temperature flow properties, and clean burn characteristics. Diesters and phthalate ester are both used commercially in this role. Many additives are carried and/or diluted by mineral oil. In several environmentally sensitive applications esters have replaced the traditional mineral oil diluents. The use of esters in this way has led to a significant improvement in the overall biodegradability of the package.

Esters may also be used as carrier fluid with chloroparaffins. As the weight of environmental legislation increases, the pressure on chloroparaffins increases. This has led to the use of higher molecular weight chloroparaffins in metalworking applications, and so on. Unfortunately, as the molecular weight of the chloroparaffin increases, its solubility in mineral oil decreases. Esters have been used to cosolubilize the chloroparaffin in the mineral oil.

10. Metalworking Fluids

Monoesters, diesters, and PAG esters are commonly used in metalworking fluids. Polyol esters, polymeric esters, and phthalates are sometimes used. The market is driven by performance, as well as handling and disposal costs.

Esters have the following advantages in this application area:

They are environmentally considerate.
They are good boundary lubricants.
They act as friction modifiers.
They are biodegradable and low in ecotoxicity.
Their good surface wetting ability lets them penetrate between the work tool and workpiece.

These properties have led to the use of esters in steel rolling, aluminum drawing, and cutting oils. Esters are starting to see some use as quenching fluids as well. Most esters have poor solubility with water. However, complex polyalkylene glycol esters that are ethoxlated are fully water soluble. These esters show synergism with corrosion inhibitors of many types.

11. Greases

Esters commonly used as greases are diesters and polyols. Phthalates and trimellitates are used, as well. Market drivers are biodegradability the need to find a white oil replacement.

Esters are used as base stocks for greases when one or more of the following properties are required:

low temperature flow (e.g., aircraft wheel bearings)
high temperature applications

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biodegradability
low toxicity (e.g., food use applications)

12. Textile Spin Finish

Esters commonly used in textile spin finish formulations are monoesters, diesters, and polyols. Also used are PAG esters and trimellitates. Market drivers are higher thermal stability, biodegradability, and lower aerosol toxicity.

Textile lubricants should fulfill the following requirements:

Good frictional properties (both fiber–fiber and fiber–metal)
Good antistatic protection (prevents filament ballooning)
Low volatility
Environmentally acceptable: (a) low aerosol toxicity, (b) high smoke point, (c) nondermatitic, and (d) easy to dispose of
Water soluble or emulsifiable
Good product stability
Nonstaining

As spin speeds, and therefore temperatures increase, there is corresponding growth in the need for low viscosity, low volatility, low deposits, and high smoke point lubricants. Esters meet all these criteria and have the advantage of being biodegradable as well.

As these requirements become ever more demanding, there is a move from monoesters and diesters toward polyol esters, which are superior in thermal stability.

13. Mold Release Oils

Esters commonly used for mold release oils in, for example, concrete, are TMP and PE oleates. Phthalates also are used in these applications.

IV. MANUFACTURERS, MARKETING, AND ECONOMICS

A. Manufacturers

Table 17 lists current ester lubricant suppliers and the types of ester they make. Typically, these plants will produce esters not only for lubricant use but for other applications as well (cosmetics, plasticizers, biodiesel, etc.). Several of these ester plants are large (. 100,000 tons), which means that there is no shortage of ester lubricant capacity. Changes in the market are occurring. Recently, ICI acquired Unichema to become the largest producer of esters into synthetic lubricants.

B. Markets

One difficulty in deciding the size of the ester lubricant market entails determining exactly what market segments should be included. For instance, should such nonlubricants as dielectric fluids, fuel additives, mold release agents, biodiesel, plasticizers, or hydraulic fluids be included? For the following estimates, only the areas discussed in the application section are counted.

Table 18 indicates the global size of the ester market, its growth rate, and its share of the market in synthetic lubricants. In several application areas polyol esters are expected to replace diesters because of the superior thermal and chemical stability of the former. Therefore, polyols show a higher growth rate than diesters.

The volume of synthetics used in engine oils has substantially increased since 1988, with annual growth rates of esters being in the region of 11%. This is due to increased use of synthetics in crankcase oils. The move toward synthetics has been entirely performance driven. Growth

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Table 17 Ester Lubricant Companies

Company	Esters produced[a]	Manufacturing locations	Trade name
ADK	5,6,7	Asia	
Akzo	3	Europe/U.S.A.	Ketjenlube
Aqualon	7	U.S.A	Hercolube
BASF	2	Europe	Glissofluid
Daihachi, Chemicals	2,4,5,6	Asia	
Exxon/Paramins	2,4,5,7	U.S.A	Jayflex/Vistol
FINA (Oleotina)	6,7	Europe	Radia
FMC (ex CIBA)	2,4,5,7	Europe	Reolube
Hatco	2,3,4,5,6,7	U.S.A.	Hatcol
Henkle/Emery	1,2,6,7	Europe/U.S.A./Asia	Edenor/Emery
Hüls	2,3,4,5,7	Europe/U.S.A.	Drivolan
ICI	2,3,4,5,7	Europe	Emkarate
Inolex		U.S.A	
INSPEC (ex-ISC)	2,5	Europe	BISOLUBE
KAO	2,4,5,6,7	Asia	
Mobil	2,7	Europe/U.S.A.	Mobil Ester
NOF	6,7	Asia	
NYCO	1,2,3,7	Europe	Nycobase
Quaker	7	Europe/U.S.A.	
Shin-Nihon Rika	2,4	Asia	
Unichema	1,2,6,7	Europe/Asia	Priolube
Union Camp	1,2,6,7	U.S.A./Europe	Uniflex
Witco		U.S.A.	Witcosyne

[a] 1, C_{36} dimerates; 2, diesters; 3, complex esters; 4, phthalates; 5, trimellitates; 6, monoesters; 7, polyols.

in synthetic engine oils outside Western Europe is now being seen in North America, Southeast Asia, Japan, and South Africa.

The growth in aviation oils is expected to follow the growth in the aviation market. Changes in growth will occur if and when new markets open up in Eastern Europe and China.

Increases in the sales of esters into the two-stroke and hydraulic fluid markets are expected to result from changes in environmental legislation. New voluntary standards for environmentally considerate hydraulic fluids have already been introduced or are being drafted in Germany (Blue Angel), some Scandinavian countries (Nordic Swan), and the United States (ASTM).

Laws will continue to tighten on the disposal of waste lubricants, resulting in an increased cost penalty for disposing of non–environmentally considerate lubricants.

Table 18 Global Ester Growth and Market Share Data

Ester type	Size in 1995 (tons × 10^3)	Growth rate (%)	Share of synthetic market (%)
Polyol and polymeric esters	97	7	15
Other esters	70	5	11

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The Montreal Protocol calls for the industrial nations to phase out R12 by 1996. This required a shift from traditional mineral oils to polyol esters in the domestic appliance sector. This shift occurred first in Europe (1992) and was shortly followed by the United States and some Pacific Rim nations. The changeover is reaching completion, but the majority of me industrial commercial market has yet to comply. This sector has until 2005 to move away from R22. It is likely that legislation will move this date forward and that many OEMs will choose to move much earlier.

The air compressor market is well established with only moderate growth expected, unless legislation further restricts the use of mineral oil.

V. OUTLOOK

Over the last decade, several general trends in lubricant properties have been seen:

higher thermal stability
improved environmental performance
longer lubricant life
improved cost-effectiveness

Esters have performance characteristics to meet all these developing trends.

As companies get larger and developing markets take off, new lubricants will be expected to be available globally. New environmental legislation and toxicity registration schemes are occurring at an ever increasing pace. The cost of registering a brand new lubricant globally could potentially run as high as several hundred thousand dollars. Such costs can potentially curtail work on radically different chemistries. One way to minimize costs is to work on polymeric materials that either have exemption under many nations' registration programs or reduced toxicity costs. Polymers also allow a great deal of chemical flexibility. This has led to considerable ester research in the areas of complex polyols, PAG esters, and polycarbonates. Research is also continuing in the more traditional diester, phthalate, and polyol ester areas as new raw materials or production routes are developed. The field of renewable resource materials is particularly fertile because it offers not only the advantage of improved environmental performance but also reduced costs.

Continued development of ester chemistry can therefore be expected to continue for at least the foreseeable future.

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